

SPECIFICATION AMENDMENTS

On page 1, insert above line 1, insert--Priority Claim

The present application claims priority on European Patent Application 02253980.3 filed 7 June 2002.--

On page 1, delete line 11-14.

Paragraph at line 15 of page 1 has been amended as follows:

-- The invention further relates to a process to prepare the catalyst or catalyst precursor from a shapeable dough, to the die-plate used for the preparation of an extruded catalyst or catalyst precursor, ~~to the use of the catalysts~~, as well as to hydrocarbons prepared by using the catalyst.--

Paragraph at line 9 of page 2 has been amended as follows:

-- It is most desirable to employ a highly efficient catalyst. In terms of the Fischer-Tropsch process, a highly efficient catalyst is one which exhibits not only a high level of activity for the conversion of carbon monoxide and hydrogen to hydrocarbons, but also a high degree of selectivity to higher molecular hydrocarbons, in particular C₅ hydrocarbons and larger, henceforth referred to as "C₅+ hydrocarbons". Preferably, the degree of branching in the C₅+ hydrocarbons should be low. It is taught in the prior art that the efficiency of a catalyst in general increases as the size of the catalyst particle decreases. Further, catalysts should show a high stability, i.e. deactivation should be very low.--

Paragraph at line 22 of page 2, ending at line 3 of page 3, has been amended as follows

-- The Fischer-Tropsch synthesis may be carried out using a variety of reaction regimes, for example a ~~fluidised~~ fluidized bed regime or a slurry bed regime. When using a process employing a fixed bed of catalyst particles, a major consideration in the design of the process is the pressure drop through the catalyst bed. It is most desirable that the pressure drop should be as low as possible. However, it is well reported in the art that, for a given shape of catalyst particles, as the size of the catalyst particles in a fixed bed is

reduced, there is a corresponding increase in pressure drop through the catalyst bed. Thus, there exists a conflict in the design of fixed catalysts beds when trying to achieve a satisfactory level of catalyst efficiency whilst while keeping the pressure drop through the bed to a minimum.--

Paragraph at line 4 of page 3 has been amended as follows:

-- In addition to the above, the catalyst particles should be sufficiently strong to avoid undesired attrition and/or breakage. Especially in fixed beds the bulk crush strength should be (very) high, as beds are used in commercial reactors of up to 15 meters high in height. Especially at the lower end of the bed the strength of the catalyst particles plays an important part role. This is an additional complication in designing further improved catalyst particles.--

Paragraph at line 20 of page 3 has been amended as follows:

-- Accordingly, there exists a need for a catalyst or catalyst precursor comprising a Group VIII element and optionally a promoter selected from the elements of Group IIA, Group IIIB, Group IVB, Group VB, Group VIB or Group VIIB of the Periodic Table of the Elements which catalyst displays a high activity and selectivity in the Fischer-Tropsch synthesis process, while keeping the pressure drop in the fixed bed as low as possible and displaying a high crush strength. ~~Further, the and stability should be very high.~~

Paragraph at line 16 of page 4 has been amended as follows:

-- A variety of shapes and designs of catalyst particles for use in the fixed bed operation of the Fischer-Tropsch synthesis have been proposed. Thus, EP-0,428,223 discloses that the catalyst particles may be in the form of cylinders; hollow cylinders, for example cylinders having a central hollow space which has a radius of between 0.1 and 0.4 of the radius of the cylinder; straight or rifled (twisted) trilobes; or one of the other forms disclosed in US-4,028,221 US Pat No 4,028,221. Trilobe extrudates are said to be preferred.--

Paragraph at line 25 of page 5 has been amended as follows:

-- ~~It has now surprisingly been found that~~ It would be useful to find specifically shaped catalyst particles or catalyst precursor particles ~~offer that offered~~ unexpected and

sizeable advantages compared with conventional "trilobal" catalyst particles, especially when used in mass transfer or diffusion limited reactions in fixed-bed reactors, for instance as catalysts in the Fisher-Tropsch process.--

Paragraph at line 1 of page 6 has been amended as follows:

-- The present invention ~~therefore relates~~ is directed to a shaped catalyst or catalyst precursor ~~containing a catalytically active component or a precursor therefor~~ therefore, the component selected from elements of Group VIII of the Periodic Table of the Elements, supported on a carrier, which catalyst or catalyst precursor is an elongated shaped particle comprising three protrusions each extending from and attached to a central position, wherein the central position is aligned along the longitudinal axis of the particle, the cross-section of the particle occupying the space encompassed by the outer edges of six circles around a central circle, each of the six circles touching two neighbouring neighboring circles whilst ~~while~~ three alternating circles are equidistant to the central circle and may be attached to the central circle, minus the space occupied by the three remaining outer circles and including the six interstitial regions.--

Paragraph at line 20 of page 6 has been amended as follows:

-- ~~It is known that the~~ The type of reactions which require solid catalyst particles are often limited by the rate of diffusion of the reactants into the catalyst particle or by the rate of diffusion of the evolving products out of the catalyst particle. This is especially true for liquid phases reactions. Accordingly, catalyst particles which display a high surface-to-volume ratio are advantageous.--

Paragraph at line 27 of page 6, ending at line 4 of page 7, has been amended as follows:

-- It has been found that the catalyst particles according to the present invention have a larger surface-to-volume ratio than corresponding conventional "trilobal" particles of similar size and suffer substantially less from pressure drop than such corresponding conventional "trilobal" particles, due to higher voidage. In addition, a good C₅+ selectivity and a good stability is obtained. An additional advantage is that the selectivity for linear (unbranched) products is increased. Further, the particles are sufficiently strong and ~~can~~ may easily be made by extrusion.--

Paragraph at line 5 of page 7 has been amended as follows:

-- The shaped catalyst particles ~~can~~ may be formed of any suitable material provided it is capable of being processed in such a way that ~~their~~ the intended shape is obtained. Methods of preparing such shapes include pressing, extruding or otherwise forcing a granular or powdered catalyst or catalyst precursor material into various shapes under certain conditions, which will ensure that the particle retains the resulting shape, both during reaction as well as during regeneration.--

Paragraph at line 14 of page 7 has been amended as follows:

-- The catalysts of the present invention, especially for use in the Fischer-Tropsch process, comprise, as the catalytically active component, a metal from Group VIII of the Periodic Table of the Elements. Particular catalytically active metals include ruthenium, iron, cobalt and nickel, more preferably cobalt. Combinations of two or more components are also possible. Preferably, a Fischer-Tropsch catalyst is used, which yields substantial quantities of paraffins, more preferably substantially unbranched paraffins. A most suitable catalyst composition for this purpose includes a cobalt-containing Fischer-Tropsch catalyst. Such catalysts are described in the literature, see e.g. AU 698392 and WO 99/34917. Preferred hydrocarbonaceous feeds for the preparation of synthesis gas are natural gas or associated gas. As these feedstocks usually result in synthesis gas having H₂/CO ratio's of close to 2, cobalt is a very good Fischer-Tropsch catalyst as the user ratio for this type of catalysts is also about 2.--

Paragraph at line 18 of page 9 has been amended as follows:

-- The suitable material for the shaped catalyst particles should be processed in such a way that ~~their~~ the intended shape is obtained. One example of a processing method is an extrusion process, wherein a shapeable dough, preferably comprising one or more sources for one or more of the catalytically active elements, and optionally one or more sources for one or more of the promoters and the finely divided refractory oxide or refractory oxide precursor is mulled together with a suitable solvent. The mulled mixture is then extruded through an orifice in a die-plate. The resulting extrudates are dried. If necessary, (additional) catalytic element sources and/or promoters may be applied to the extrudates by impregnation. Other processes which may be used are palletizing and pressure ~~moulding~~ molding.--

Paragraph at line 8 of page 10 has been amended as follows:

-- The use of specific die-plates enables the formation of the intended shape of the catalyst particles. Die-plates are well known in the art and ~~can~~ may be made from metal or polymer material, especially a thermoplastic material.--

Paragraph at line 13 of page 10 has been amended as follows:

-- Preferred catalyst particles according to the present invention have a cross-section in which the three alternating circles (forming part of the outer circles) have diameters in the range of between 0.74 and 1.3 times the diameter of the central circle, preferably between 0.87 and 1.15 times the diameter of the central circle.--

Paragraph at line 3 of page 11, ending at line 9 of page 12, has been amended as follows:

-- In ~~Figure Fig.~~ 1 a cross-sectional view of the most preferred particles according to the invention has been depicted. The surface of the cross-sectional shape is (indicated by the solid line). ~~can be described as defined in the main claim.~~ It will be clear from ~~this Figure Fig.~~ (depicting the cross-section of the preferred particles) that in the concept of six circles of equal size aligned around a central circle of the same size each outer circle borders its two ~~neighbour~~ neighbor circles and the central circle ~~whilst while~~ subtraction of three alternating outer circles (indicated by the dotted line) provides the remaining cross-section, built up from four circles (the central circle and the three remaining alternating outer circles) together with the six areas formed by the inclusions of the central circle and six times two adjacent outer circles. These areas are referred to as "interstitial areas". The three remaining alternating outer circles are equidistant to the central circle. The term "equidistant" as used herein refers to the circumstance that the distance between the ~~centre~~ center of the central circle to the ~~centre~~ center of one of the outer circles is equal to the distance between the ~~centre~~ center of the central circle to the centre of either one of the other remaining outer circles. For the purpose of this application specification the term "equidistant" may comprise deviations up to 20% of the distance, preferably up to 10%, more preferably up to 5%. In the most preferred embodiment there is no deviation. The circumference of the preferred shaped particles according to the present invention is such that it does not contain sharp corners, which can also be expressed as the derivative of the cross-section being continuous. The diameter of the particles (the most preferred particles in accordance with the present invention) is defined as the distance

between the tangent line that touches two protrusions and a line parallel to this tangent line that touches the third protrusion. It is indicated as d_{nom} in ~~Figure~~Fig. 1. In the case that the three alternating circles have one or two different diameters, d_{nom} is the sum of the three measured diameters divided by three.--

Paragraph at line 1 of page 12 has been amended as follows:

-- The three protrusions and the central position together form the cross-section of the catalyst or catalyst precursor. The main part of each protrusion is formed by one of the (remaining) alternating circles. The main part of the central protrusion is formed by the central circle. The interstitial areas are divided between the central position and the protrusion by a line perpendicular to the line connecting the ~~centre~~ center point of the central circle and the ~~centre~~ center part of the alternating circle. The perpendicular line (dotted line) crosses the connecting line (solid line) at a point exactly in the middle between the two ~~centre~~ center points (see ~~figure~~ Fig. 2).--

Paragraph at line 22 of page 12 has been amended as follows:

--It will be clear that minor deviations from the shape as defined are considered to be within the scope of the present invention. In the case where the catalyst or catalyst precursor of the present invention is prepared by an extrusion process, die-plates are used. It is known to those skilled in the art to manufacture die-plates having one or more holes in the desired shape of the particles, in this case according to the present invention, and which ~~tolerances~~Tolerances may can be expected in practice when producing such die-plates. In this respect it is observed that the pressure release immediately after extrusion may result in deformation of the extrudates. Usually the minor deviations are within 10%, preferably within 5%, more preferably within 2% of d_{nom} with respect to the ideal shape as defined in the present invention.--

Paragraph at line 13 of page 13 has been amended as follows:

-- It is possible to produce catalyst particles according to the present invention, which also contain one or more holes along the length of the particles. For instance, the particles can contain one or more holes in the area formed by the central cylinder (the central circle in the cross-section given in Figure Fig. 1) and/or one or more holes in one or more of the alternating cylinders (the alternating circles in the cross-section given in Figure

Fig. 1). The presence of one or a number of holes causes an increase of the surface to volume ratio which in principle allows exposure of more catalytic sites and, in any case, more exposure to incoming charges which may work advantageously from a catalytic point of view. Since it becomes increasingly difficult to produce hollow particles as their size becomes smaller it is preferred to use porous particles without holes when smaller sizes are desired for certain purposes.--

Paragraph at line 10 of page 14 has been amended as follows:

--The catalyst particles according to the present invention ~~can~~ may be described as having a length/diameter ratio (L/D) of at least 1. The particles according to the present invention ~~can~~ may have a L/D in the range between 1 and 25. Preferably, the particles according to the present invention have a L/D in the range between 1.5 and 20, more preferably in the range between 2 and 10. For example, the particles used in the experiment to be described hereinafter had a L/D of about 2.5.--

Paragraph at line 23 of page 14, ending at line 20 of page 15 has been amended as follows:

-- The catalytic conversion process may be performed under conventional synthesis conditions known in the art. Typically, the catalytic conversion may be effected at a temperature in the range of from 150 °C to 300 °C, preferably from 180 °C to 260 °C. Typical total pressures for the catalytic conversion process are in the range of from 1 bar to 200 bar absolute, more preferably from 10 bar to 70 bar absolute. In the catalytic conversion process especially more than 75 wt% of C₅+, preferably more than 85 wt% C₅+ hydrocarbons are formed. In a typical conversion process using a catalyst according to the present invention, the amount of products comprising one or more tertiary substituted carbon atoms (henceforth referred to as "branched" products) is may be at least 20% less compared to a conversion process with similar reaction conditions, where a conventional trilobal catalyst is used. Depending on the catalyst and the conversion conditions, the amount of heavy wax (C₂₀+) may be up to 60 wt%, sometimes up to 70 wt%, and sometimes even up ~~till~~ to 85 wt%. Preferably a cobalt catalyst is used, a low H₂/CO ratio is used (especially 1.7, or even lower) and a low temperature is used (190-230 °C). To avoid any coke formation, it is preferred to use an H₂/CO ratio of at least 0.3. It is especially preferred to carry out the Fischer-Tropsch reaction under such conditions that the SF-alpha

value, for the obtained products having at least 20 carbon atoms, is at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955. Preferably the Fischer-Tropsch hydrocarbons stream comprises at least 35 wt% C₃₀+, preferably 40 wt%, more preferably 50 wt%.--

Paragraph at line 3 of page 16 has been amended as follows:

-- The catalyst particles described herein can also be formed as helical lobed particles. The term helical lobed particles as used herein refers to an elongated shaped particle comprising three protrusions each extending from and attached to a central position, the central position being aligned along a longitudinal axis, the particle having a cross-section occupying the space encompassed by the outer edges of six circles around a central circle, each of the six circles bordering two ~~neighbouring~~ neighboring circles whilst while three alternating circles are equidistant to the central circle and may be attached to the central circle, minus the space occupied by the three remaining outer circles and including the six interstitial regions, which protrusions extend along and are helically wound about the longitudinal axis of the particle.--

Paragraph at line 18 of page 16 has been amended as follows:

-- By employing helical lobed particles, a larger diameter helical lobed catalyst particle ~~can~~ may be employed to achieve a given selectivity than is necessary when employing straight lobed particles, resulting in a greater reduction in pressure drop across the catalyst bed than expected from the prior art. Alternatively, for a given design of fixed bed with a predetermined pressure drop, by employing the helical lobed particles in the Fischer-Tropsch process a substantially higher selectivity ~~can~~ may be achieved than with the appropriate straight lobed particles necessary to meet the pressure drop requirements.--

Paragraph at line 32 of page 16, ending at line 3 of page 17, has been amended as follows:

-- Experiments were carried out to monitor the Fischer-Tropsch process using catalyst particles made up of trilobe-shaped extrudates (comparative example) and using catalyst particles ~~having a shape as defined in claim 1~~ according to the invention (working examples).--

Paragraph at line 11 of page 18 has been amended as follows:

-- Following reduction, the pressure was increased to 32 bara (STY 140) or 57 bara (STY 180). The reaction was carried out with a mixture of hydrogen and carbon monoxide. The space time yield (STY), expressed as ~~grammes~~ grams hydrocarbon product per litre liter catalyst particles (including the voids between the particles) per hour, the C₅+ selectivity, expressed as a weight percentage of the total hydrocarbon product, and the ratio of unsaturated product versus saturated product for products having between 2 and 4 hydrocarbons were determined for each experiment after 50 hours of operation. The results are set out in Table I.--

Paragraph at line 13 of page 19 has been amended as follows:

--Catalysts A, C, D and E were tested in a process for the preparation of hydrocarbons. Micro-flow reactors containing 10 ml of catalyst extrudates A, C, D and E, respectively, in the form of a fixed bed of catalyst particles, were heated to a temperature of 260 °C, and ~~pressurised~~ pressurized with a continuous flow of nitrogen gas to a pressure of 2 bar abs. The catalysts were reduced in-situ for 24 hours with a mixture of nitrogen and hydrogen gas. During reduction, the relative amount of hydrogen in the mixture was gradually increased from 0% to 100%. The water concentration in the off-gas was kept below 3000 ppmv.--

Paragraph at line 25 of page 19, ending at line 4 of page 20, has been amended as follows:

-- Following reduction, the pressure was increased to 26 bar abs. The reaction was carried out with a mixture of hydrogen and carbon monoxide. The reaction temperature is expressed as the weighted average bed temperature (WABT) in °C. The space time yield (STY), expressed as ~~grammes~~ grams hydrocarbon product per litre liter catalyst particles (including the voids between the particles) per hour, the C₅+ selectivity, expressed as a weight percentage of the total hydrocarbon product, and the ratio of unsaturated product versus saturated product for products having between 2 and 4 hydrocarbons were determined for each experiment after 50 hours of operation. The results are set out in Table II.

On page 21, above line 1, insert --We claim:--